In-situ Corrosion Testing of Selected HLW Container Materials under the Conditions of the HLW Test Disposal in the Asse Salt Mine

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FORSCHUNGSZENTRUM KARLSRUHE
Technik und Umwelt

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Summary

In the framework of the HLW test disposal (HAW-project) in the Asse salt mine, the long-term corrosion behavior of potential HLW container materials was investigated under conditions simulating the long-term disposal phase in a borehole. The materials investigated were: The corrosion resistant (passively corroding) materials Ti 99.8-Pd, Hastelloy C4, Nickel and Cr-Nr steel 1.4833, and the corrosion allowance (actively corroding) TStE 355 carbon steel. Specimens of the above-mentioned materials were stored for about five years in an electrically heated cased borehole at temperatures between 170°C and 190°C. The casing consisted of steel with corrosion protection of Ti 99.8-Pd. During the test duration, the specimens were exposed to water/brine and gases (mainly CO_2, CH_4 and H_2) released from the rock salt or generated by corrosion (H_2).

The corrosion results indicate that the alloy Ti 99.8-Pd is highly resistant to pitting and crevice corrosion, and its general corrosion rate is negligible low (< 0.1 µm/a). Nickel is subjected to non-uniform general corrosion, and its corrosion rate (13 µm/a) is clearly higher than that of Ti 99.8-Pd. The Cr-Ni steel 1.4833 investigated suffers from severe pitting corrosion and stress corrosion cracking. Therefore, the Cr-Ni steels must be excluded as material for long-lived containers. The Cr-Ni-Mo alloy Hastelloy C4 shows a high resistance to general corrosion, but the formation of some small pits on the specimen surface was observed. For this reason there is some doubt about the suitability of Hastelloy C4 as container material.

The corrosion allowance (actively corroded) material carbon steel TStE 355 shows a good resistance to pitting and crevice corrosion, and its general corrosion rates (13-37 µm/a) imply corrosion allowance acceptable for thick-walled containers. In view of these results, the alloy Ti 99.8-Pd and the carbon steels continue to be considered as the most promising materials for the realization of the corrosion resistant and corrosion allowance container concept, respectively. Further in-depth corrosion studies on these materials are in progress.

In-situ Korrosionsuntersuchungen an ausgewählten HAW-Behälterwerkstoffen unter den Bedingungen der HAW-Versuchseinlagerung im Salzbergwerk Asse

Zusammenfassung

Im Rahmen des HAW-Projektes im Salzbergwerk Asse wurde das Korrosionsverhalten potentieller HAW-Behälterwerkstoffe unter Bedingungen untersucht, wie sie längerfristig in einem Einlagerungsbohrloch zu erwarten sind. Untersucht wurden die korrosionsresistenten (passiv korrodierenden) Werkstoffe Ti 99.8-Pd, Hastelloy C4, Nickel und Cr-Ni Stahl 1.4833 und der korrosionszulassende (aktiv korrodierende) Feinkornbaustahl TStE 355. Zur Simulation der Endlagerbedingungen wurden Proben aus den oben genannten Werkstoffen fünf Jahre in einem elektrisch beheizten, verrohrten Bohrloch bei Temperaturen zwischen 170°C und 190°C ausgelagert. Das Verrohrungsmaterial war unlegierter Stahl versehen mit einem Korrosionsschutz aus Ti 99.8-Pd. Während der Versuchszeit waren die Proben dem Angriff von Wasser/Salzlösung und Gasen wie CO_2, CH_4 und H_2 ausgesetzt, die aus dem Steinsalz freigesetzt oder durch Korrosion (H_2) gebildet wurden.

Unter den Prüfbedingungen zeigt die Legierung Ti 99.8-Pd eine sehr hohe Beständigkeit gegenüber Loch- und Spaltkorrosion und ihre Flächenkorrosion ist vernachlässigbar klein (< 0.1 μm/a). Bei Nickel ist eine ungleichmäßige Flächenkorrosion festzustellen und seine Korrosionrate (13 μm/a) ist deutlich höher als bei Ti 99.8-Pd. Der hochlegierte Cr-Ni-Stahl 1.4833 zeigt eine hohe Empfindlichkeit gegenüber Loch- und Spannungsrißkorrosion und muß deshalb als Werkstoff für einen langzeitbeständigen Behälter ausgeschlossen werden. Die Cr-Ni-Mo Legierung Hastelloy C4 weist eine hohe Resistenz gegenüber Flächenkorrosion auf, jedoch wurde bei einigen Proben die Bildung von kleinen Löchern beobachtet. Aus diesem Grunde muß die Eignung von Hastelloy C4 als Behälterwerkstoff bezweifelt werden.

Der aktiv korrodierte unlegierte Feinkornbaustahl TStE 355 (korrosionszulassendes Material) zeigt eine gute Beständigkeit gegenüber Loch- und Spaltkorrosion und seine Flächenkorrosion (13-37 μm/a) führt zu technisch akzeptablen Korrosionszuschlägen für dickwandige Behälter. Angesichts dieser Ergebnisse werden die Legierung Ti 99.8-Pd und unlegierte Stähle weiterhin als die aussichtsreichsten Materialien für die Realisierung eines korrosionsresistenten bzw. korrosionszulassenden HAW-Behälters betrachtet. Weitergehende Untersuchungen sind im Gange.

Table of Contents **Page**

1. INTRODUCTION

According to the German waste disposal concept, the heat-generating nuclear waste such as vitrified high-level waste and spent fuel will be disposed of in repositories located in deep rock-salt formations. The isolation of the radio-nuclides from the biosphere shall be ensured by a combination of geological and engineered barriers. One element of this multi-barrier concept is the waste packaging. Consequently, studies have been undertaken at KfK within the frame-work of the European Community research programme to qualify materials for long-lived packagings that could serve as a radionuclide barrier during the elevated-temperature phase in the disposal area, which lasts a few hundred years. The main requirement made on the packaging materials is their corrosion resistance in rock salt and salt brines. Salt brines in the disposal area may originate from the thermal migration of brine inclusions in the rock salt and have to be considered in accident scenarios, e.g. brine inflow through an anhydride layer.

In previous comprehensive corrosion studies [1,2] on a large number of materials in salt brines, three materials were identified as promising for the manufacturing of long-lived containers (overpacks) surrounding the Cr-Ni steel waste canisters. These are: The passively corroding alloys Ti 99.8-Pd and Hastelloy C4 as reference materials for a corrosion resistant concept and the actively corroding carbon steels as reference materials for a corrosion allowance concept. To characterize the long-term corrosion behavior of these materials in more detail, further laboratory-scale and in-situ corrosion studies are being performed. In the present work, long-term in-situ corrosion experiments (field experiments) were performed in the Asse salt mine in the framework of the HLW test disposal [3]. Besides the materials Ti 99.8-Pd, Hastelloy C4 and the unalloyed steel TStE 355, a selected Cr-Ni steel and pure Nickel were examined. The materials were investigated under conditions simulating the long-term disposal phase in a borehole. These conditions will take place after the complete sealing of the waste containers by the creeping salt. For this purpose, corrosion specimens of the above-mentioned materials were stored for about five years in a electrically heated cased borehole. After termination of the heater test, the specimens were recovered and subjected to post-test examination for corrosion attacks.

2. MATERIALS AND EXPERIMENTAL PROCEDURE

Five materials were investigated in the framework of the HAW-project. These are: The three most promising container materials unalloyed fine-grained steel TStE 355, Hastelloy C4 and Ti 99.8-Pd [4], the Cr-Ni steel 1.4833 as potential canister material for vitrified HLW, and pure Nickel. The examination of Nickel was performed in order to complete the results available so far. The chemical composition of the materials is given in Tab. 1. All materials were examined in the hot-rolled condition. For the corrosion testing, plane specimens having the dimensions 40 mm x 20 mm x 3 mm were used.

Detailed information on the HAW-project, the experimental conditions and the in-situ measurements is given in [5,6]. In this paper only the aspects concerning the corrosion studies are described. Briefly, the specimens were stored in a 15 m deep cased and electrically heated borehole (Type B, see [6]) at the 800 m level in the Asse salt mine under conditions which represent the long-term phase in a disposal borehole. These conditions are established after the rock salt has come into contact with the HLW containers due to the thermally induced borehole convergence. To simulate these conditions, the specimens were installed on the borehole casing (steel coated with Ti 99.8-Pd), and the initial annulus between the casing and the borehole wall was empty so that the creeping salt could come into contact with the casing surface. The specimens were located on the external wall of the casing at three vertical levels, i.e., near the top, center and bottom of the 5 m heated zone. Fig. 1 shows a vertical section of the test assembly for the HLW test disposal with indication of the specimens location. The specimens on the casing wall were fixed in ceramic insulated pockets provided in the coupling sleeves of the casing (Fig. 2).

3. TEST CONDITIONS

The test duration was about 5.3 years. During this period the corrosion specimens were exposed to the atmosphere at the interface between the borehole casing and the salt. To characterize this atmosphere, a number of in-situ measurements were performed by GSF and partners [6,7]. These include: The measurement of the temperature at various positions, and the thermally induced release of water and gas components contained in the salt or generated by corrosion (e.g. H_2).

The temperature measurements on the borehole casing [7] show that during the first 2-3 months the corrosion specimens were exposed to temperatures between about 260°C (center of the heated zone) and 240°C (near the top of the heated zone). After this short time period, however, the temperatures dropped to 170°C-190°C and remained constant during the whole test duration of about 5.3 years. Samples of the gas phase in the annular gap between the borehole casing and the salt show that during the test duration gases were released from the rock salt or generated by corrosion. The major gas components that were detected are CO_2, CH_4 and H_2 [6]. In addition, oxygen was found. After long test duration, oxygen concentrations close to that in air were detected which points to an untightness of the borehole. The maximum gas pressure measured in the borehole was about 0.2 MPa. Besides gases, a release of totally 1.1 l H_2O from the rock salt into the emplacement borehole was detected after the test duration of about 5.3 years [7].

After termination of the heater test, the specimens were recovered and subjected to post-test examination for general and local corrosion. General corrosion was calculated from the gravimetrically determined integral weight losses and the material density. The examination for local corrosion was made by microscopic evaluation, measurements of pit depth, surface profilometry and metallography. Additional information on the corrosion mechanism was obtained from the analysis of the corrosion products by means of X-ray diffraction (XRD).

4. RESULTS

The integral weight losses and the general corrosion rates of the material specimens located near the top, center, and bottom of the heated zone are compiled in Tab 2. The values are average values of four specimens. The materials Ti 99.8-Pd and Hastelloy C4 corrode, as expected, at extremely small rates (< 0.1 μm/a) under the in-situ testing conditions. Also for the Cr-Ni steel 1.4833 and Nickel the corrosion rates of 0.3-0.7 μm/a and 1.2-1.6 μm/a, respectively, are very small. The corrosion allowance material TStE 355 fine-grained steel shows the highest corrosion rates of all materials investigated. However, the values determined of 13-37 μm/a (depending on the location of the specimens) imply corrosion allowances acceptable for thick-walled containers.

The examination of Tab. 2 shows clearly differences between the corrosion rates of the TStE 355 steel at the various locations. It appears that there is a location effect on the corrosion of the steel. In general, the greatest corrosion rate of about 37 μm/a occurred on the specimens located near the bottom of the heated zone, while the smallest of 13 μm/a was observed on the specimens located near the top of the heated zone. Similar observations were made also in previous work [8].

A possible explanation for the smaller corrosion of the steel specimens near the top of the heated zone is the lowering of the brine level in the borehole during the test duration due to water consumption by the corrosion reaction with Fe. This means that the specimens near the top of the heated zone were not exposed to brine during the entire test period. Moreover, also specimens located at the same vertical level of the heated zone show significant differences in the weight losses among one another. This indicates that some specimens were exposed to a larger brine volume than others. This is attributed to a irregular distribution of the brine in the annular gap of the borehole as a consequence of a non-uniform convergence of the rock salt. A statement about a location effect on the corrosion of the other materials (Ti 99.8-Pd, Hastelloy C4 etc.) is not possible. This is due to the fact that the differences between the corrosion rates of the materials from location to location are very small, and they lie within the range of the values of the standard deviation.

To evaluate the resistance of the materials to local corrosion, all specimens were examined by surface profilometry and metallography. In addition to the material coupons, also selected specimens of the Ti 99.8-Pd corrosion protection material for the borehole casing were investigated for corrosion attacks. Figures 3-11 show characteristic optical micrographs of the materials after testing under the in-situ conditions. It is evident from the surface profiles and the metallographic examinations (Figs. 3-4) that the material Ti 99.8-Pd is completely resistant to local corrosion such as pitting or crevice corrosion. This result reflects the excellent stability of the passive film (mainly TiO_2) on this alloy in water and chloride-containing solutions, and it is in good agreement with previous results obtained in laboratory-scale investigations [4].

In the case of Hastelloy C4 (Fig. 5), some small shallow pits were observed on the specimen surface. The pits presumably occur because of localized breakdown of

the passive surface film (NiO or Cr_2O_3) in the crevice formed between Hastelloy specimen and borehole salt wall. However, crevice corrosion does not appear to be a serious problems for Hastelloy C4 because the maximum depth of the pits after 5.3 years was about only 5-10 μm. The Nickel specimens show after 5.3 years in-situ testing a non-uniform general corrosion accompagnied with shallow pits having a maximum depth of about 70 μm (Fig. 6). This gives an average penetration rate of about 13 μm/a which is clearly higher than that of the Cr-Ni-Mo alloy Hastelloy C4 (1-2 μm/a).

The specimens of the Cr-Ni steel 1.4833 (Figs. 7-8) exhibit pitting corrosion and stress corrosion cracking. This result confirms the finding of previous laboratory-scale investigations in salt brines at the high temperature of 170°C [4]. The maximum pit depth observed on the Cr-Ni-steel specimens after 5.3 years is about 200 μm. The examination of specimens made of the unalloyed TStE 355 fine-grained steel shows that this steel is resistant to pitting or crevice corrosion. The optical micrographs of specimens in Figs. 9-11 show that the carbon steel is subjected to non-uniform general corrosion, and that the greatest corrosion attack occurs at the specimens located near the bottom of the heated zone. However, the maximum penetration depth of this uneven corrosion attack corresponds to the values of the gravimetrically determined average thickness reduction of the specimens.

After the in-situ testing, the surface of the steel specimens was covered with red-brown corrosion productrs. X-ray analyses have shown that the corrosion products consist of α-Fe_2O_3 (haematite). In some specimens, Fe_3O_4, α-FeOOH (goethite) and NaCl were found, in addition to Fe_2O_3.

5. CONCLUSIONS

Among the corrosion resistant materials investigated (Ti 99.8-Pd, Hastelloy C4, Nickel, Cr-Ni steel) is the passively corroded Ti 99.8-Pd the most promising material for the realization of a corrosion resistant container concept. Under the in-situ test conditions simulating the long-term disposal phase in a HLW borehole, this alloy is completely resistant to pitting and crevice corrosion, and its general corrosion rate (< 0.1 μm/a) is negligible small. This is true both for the Ti 99.8-Pd coupons and the Ti 99.8-Pd welded sheet which was used as corrosion

protection for the borehole casing. This result confirms the findings of previous investigations.

Compared to Ti 99.8-Pd, Nickel exhibits a higher non-uniform general corrosion (13 μm/a). The Cr-Ni steel 1.4833 must be excluded as material for long-lived containers because of its high susceptibility to pitting and stress corrosion cracking. This is true for all Cr-Ni steels [4]. The Cr-Ni-Mo alloy Hastelloy C4 exhibits under the test conditions a excellent resistance to general corrosion, but a breakdown of the passive layer and the formation of some small pits was observed. Therefore, there is some doubt over its long-term behavior to pitting corrosion, particularly in $MgCl_2$-rich brines and in the presence of strong oxidants in which severe pitting was observed in previous work.

The results obtained for the unalloyed TStE 355 steel continue to support the feasibility of using carbon steels as material for corrosion allowance containers. Under the test conditions the steel exhibits a good resistance to pitting or crevice corrosion, and its general corrosion rates (13-37 μm/a) imply corrosion allowances acceptable for thick-walled containers. Further corrosion studies on Ti 99.8-Pd and carbon steels are in progress. The focus above all on the clarification of the role of high-temperature ($\leq$ 200°C) during corrosion under gamma irradiation and the determination of the influence of salt impurities (e.g. S^{2-}, $B(OH)_4$) on corrosion.

6. REFERENCES

[1] G.P. Marsh, G. Pinard-Legry, E. Smailos et al. "HLW Container Corrosion and Design", Proc. of the Second European Community Conference on Radioactive Waste Management and Disposal, Luxembourg, April 22-26, 1985, p. 314.

[2] E. Smailos, W. Schwarzkopf, R. Köster, K.H. Grünthaler, "Advanced Corrosion Studies on Selected Packaging Materials for Disposal of HLW Canisters in Rock Salt", Proc. of the Symposium on Waste Management 1988 at Tucson, Arizona, USA, February 28-March 3, 1988, Vol. 2, p. 985.

[3] K. Kühn, T. Rothfuchs, "In-Situ Experiments on the Disposal of High-Level Radioactive Wastes at the Asse Salt Mine, Federal Republic of Germany", Proc. of Waste Management'89, Tucson, Arizona, February 26 - March 2, 1989, Vol. 1, p. 567 (1990).

[4]   E. Smailos, W. Schwarzkopf. R. Storch, "Corrosion Studies on Packaging Materials for High-Level Waste Disposal in a Rock-Salt Repository", P.J. Tunturi [Ed.], Proc. of the 12th Scandinavian Corrosion Congress and EUROCORR'92, Espoo, SF, May 31 - June 4, 1992, Vol. II, p. 327. The Corrosion Society of Finland, 1992.

[5]   T. Rothfuchs, L. Vons, M. Raynal, J.C. Major, I. Müller-Lyda, "The HAW-Project: Test Disposal of Highly Radioactive Radiation Sources in the Asse Salt Mine", EUR 14531 EN (1993).

[46   T. Rothfuchs, L. Vons, M. Raynal, J.C. Major, I. Müller-Lyda, "The HAW-Project: Test Disposal of Highly Radioactive Radiation Sources in the Asse Salt Mine", Progress Report July-December 1993, Institut für Tieflagerung des Forschungszentrums für Umwelt und Gesundheit, GmbH., Report IfT 2/94 (1994).

[7]   T. Rothfuchs, GSF-IfT, unpublished results.

[8]   E. Smailos, B. Fiehn, J.A. Gago, I. Azkarate, "Corrosion studies on Selected Metallic Materials for Application in Nuclear Waste Disposal Containers", KfK 5309 (1994).

Table 1: Chemical composition of the materials examined in the HLW test field in the Asse salt mine

Material	Composition (wt.%)								
	Cr	Ni	Mo	Ti	Pd	C	Si	Mn	Fe
Ti 99.8-Pd (Mat.No. 3.7025	-	-	-	Bal.	0.17	0.01	-	-	0.05
Hastelloy C4 (Mat.No. 2.4610)	16.8	Bal.	15.9	0.33	-	0.006	0.05	0.09	0.05
Nickel	-	99.9	-	-	-	-	-	-	-
Cr-Ni steel (Mat.No. 1.4833)	23	15	-	-	-	0.08	1.0	2.0	Bal.
Fine-grained steel (TStE 355, 1.0566)	-	-	-	-	-	0.17	0.44	1.49	Bal.

Table 2:   General corrosion[+] of the materials tested in-situ under the conditions of the HLW test disposal (rock salt + limited amounts of brine; T = 170°C-190°C; t = 5.3 years)

Material	Location of the specimens					
	Top		Center		Bottom	
	Weight loss (g/m^2)	Corrosion rate ($\mu m/a$)	Weight loss (g/m^2)	Corrosion rate ($\mu m/a$)	Weight loss (g/m^2)	Corrosion rate ($\mu m/a$)
Ti 99.8-Pd	0.27 ± 0.02	0.01 ± 0.001	0.156 ± 0.09	0.006 ± 0.003	0.185 ± 0.07	0.008 ± 0.003
Hastelloy C4	0.33 ± 0.21	0.007 ± 0.005	0.30 ± 0.15	0.007 ± 0.004	0.98 ± 0.33	0.021 ± 0.007
Cr-Ni steel (1.4833)	13.6 ± 7.2	0.3 ± 0.2	30.4 ± 16.4	0.7 ± 0.4	26.5 ± 2.4	0.6 ± 0.1
Nickel	60.4 ± 16.6	1.3 ± 0.3	55.4 ± 32.8	1.2 ± 0.7	73.7 ± 5.1	1.6 ± 0.1
Fine-grained steel TStE 355	211.7 ± 80.9	12.8 ± 4.9	393.5 ± 339	23.8 ± 20.5	615.9 ± 355	37.2 ± 21.5

[+] average values of four specimens
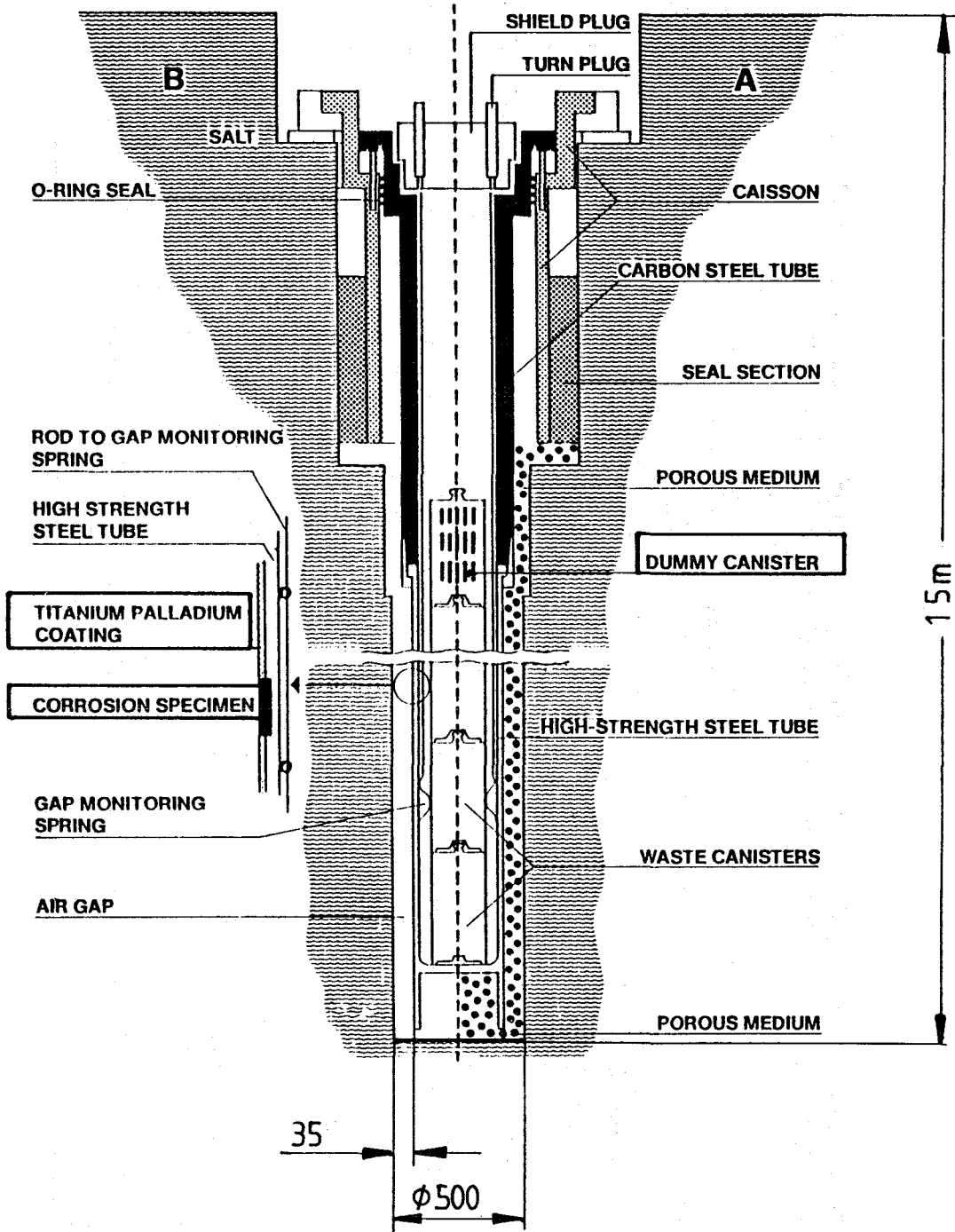
Fig. 1:   Vertical section of test assembly for the HLW test disposal with indication of the specimens location
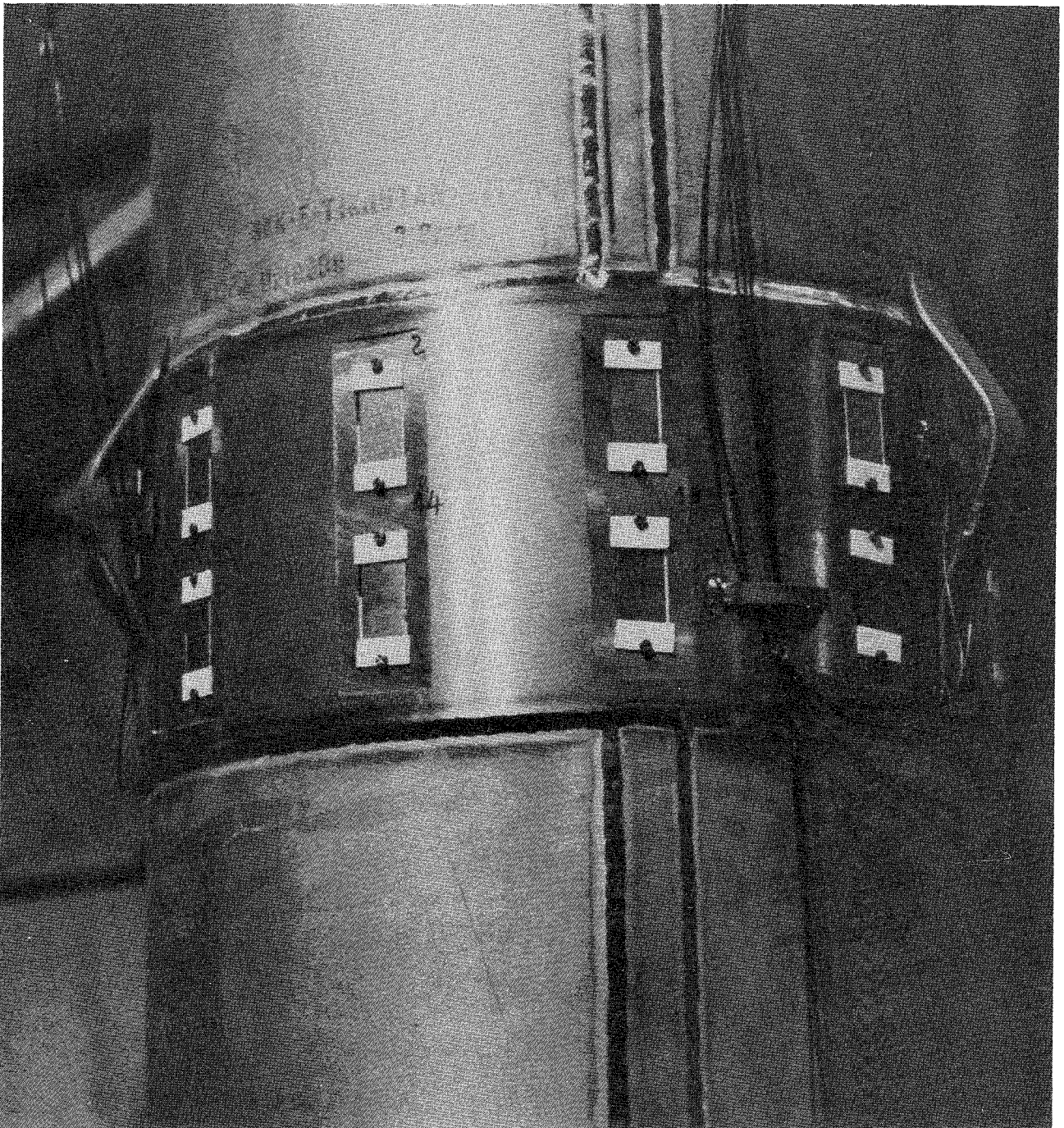
Fig. 2: Fixation of the corrosion specimens on the borehole casing before storage in the HLW test borehole
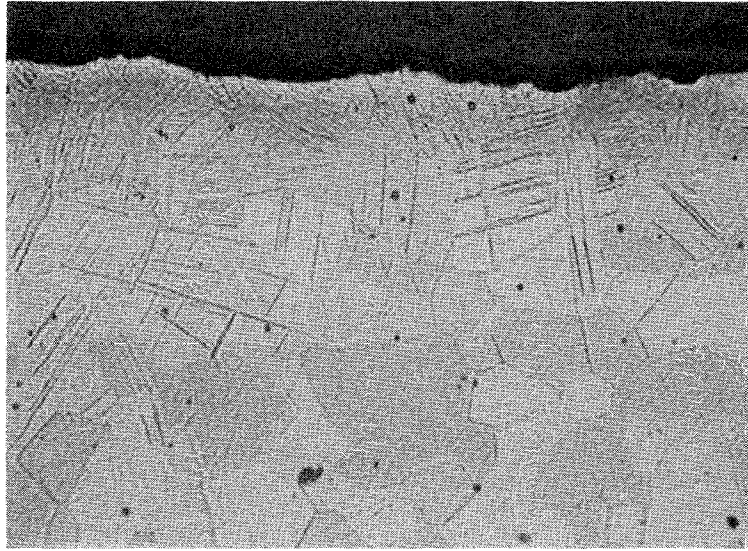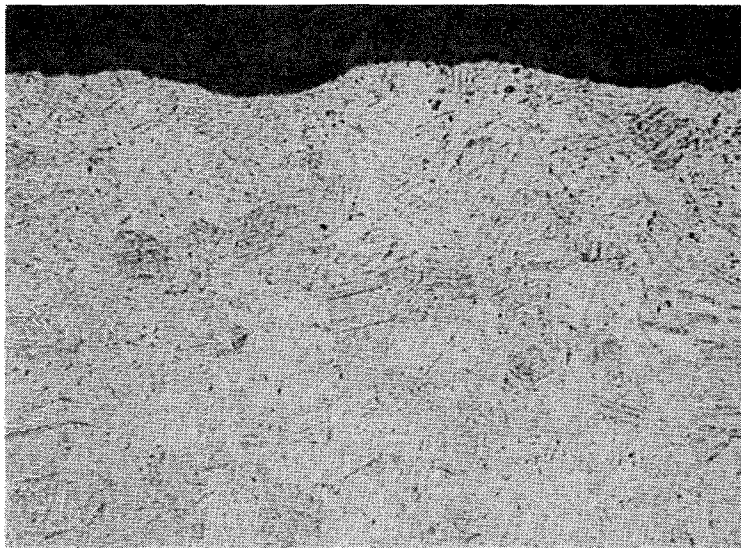
Fig. 3: Ti 99.8-Pd specimen (x 200)

Fig. 4: Ti 99.8-Pd casing material (x 200)

Figs. 3-4: Optical micrographs of Ti 99.8-Pd after storage in the HLW test borehole (rock salt + brine; T=170°C-190°C; t=5.3a)
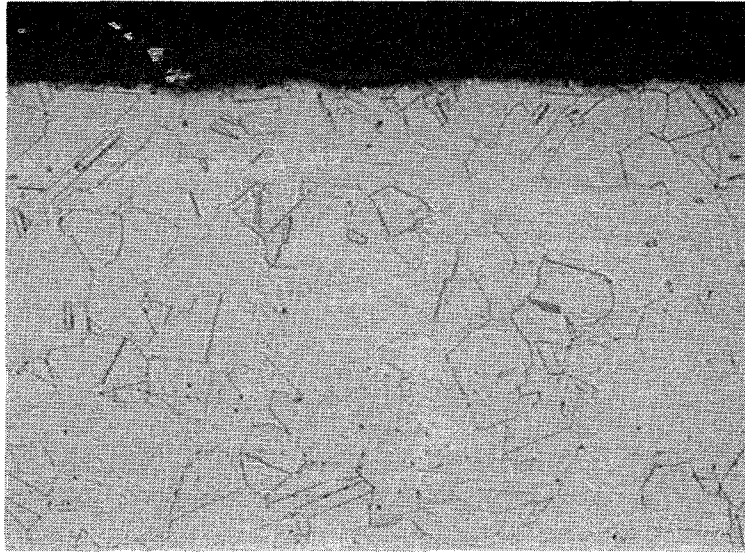
Fig. 5: Hastelloy C4 (x 200)
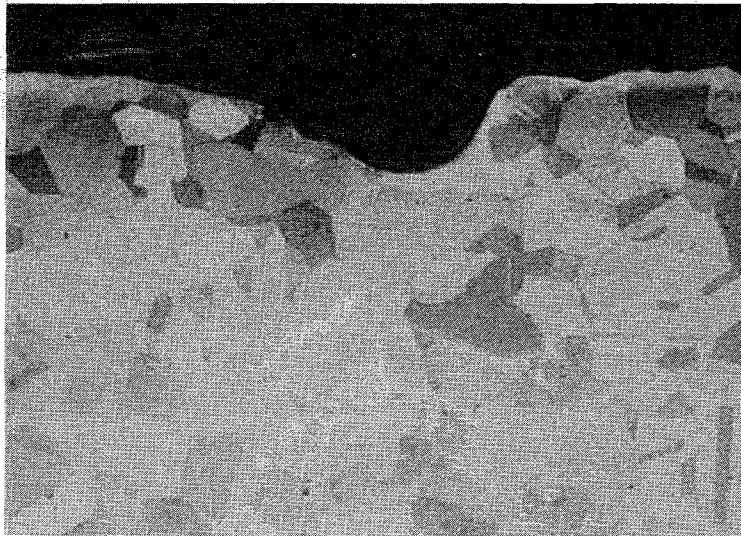
Fig. 6: Nickel (x 200)

Figs. 5-6: Optical micrographs of Hastelloy C4 and Nickel after storage in the HLW test borehole (rock salt + brine; T=170°C-190°C; t=5.3a)
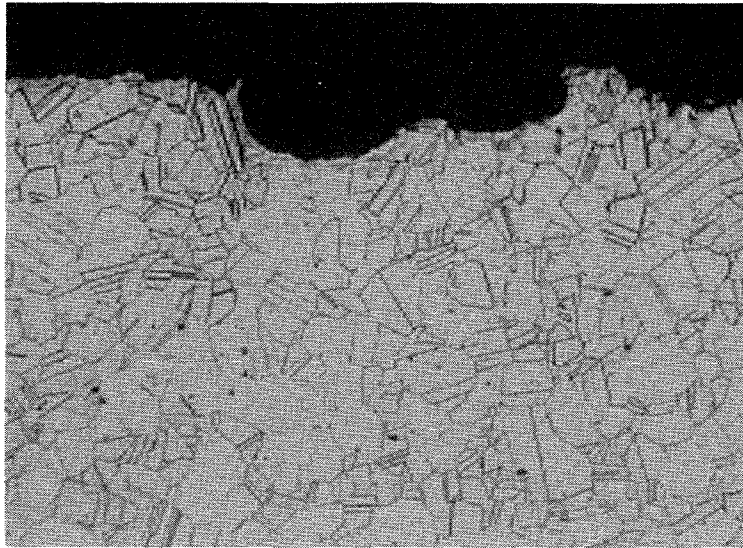
Fig. 7: Cr-Ni steel 1.4833 (x 200)
(pitting corrosion)
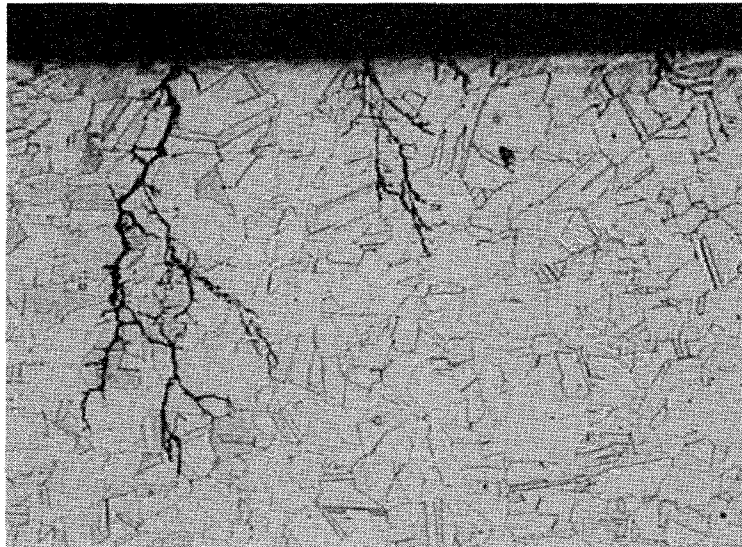
Fig. 8: Cr-Ni steel 1.4833 (x 200)
(stress corrosion cracking)

Figs. 7-8: Optical micrographs of the Cr-Ni steel 1.4833 after storage in the
HLW test borehole (rock salt + brine; T=170°C-190°C; t=5.3a)
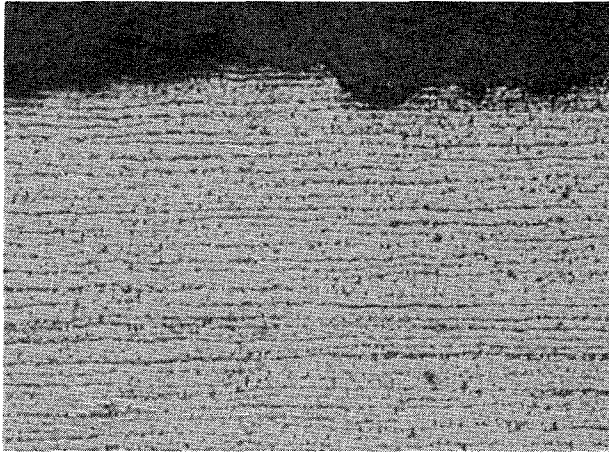
Fig. 9:   Specimen located near the top
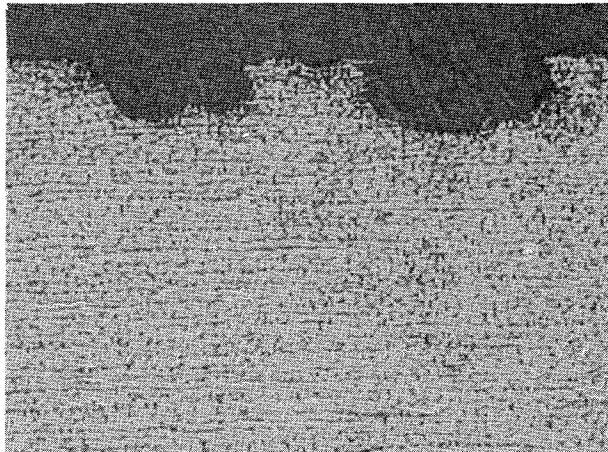   of the heated zone (x 100)

Fig. 10: Specimen located near the
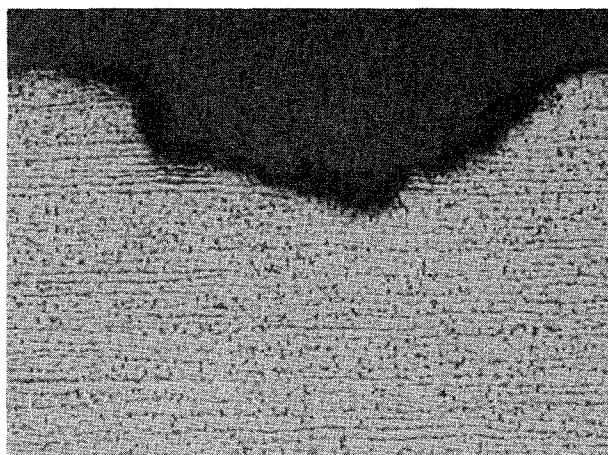   center of the heated zone
          (x 100)

Fig. 11: Specimen located near the bot-
          tom of the heated zone (x 100)

Figs. 9-11: Optical micrographs of fine-grained steel specimens after storage in
             the HLW test borehole (rock salt + brine; T= 170°C-190°C; t=5.3 a)